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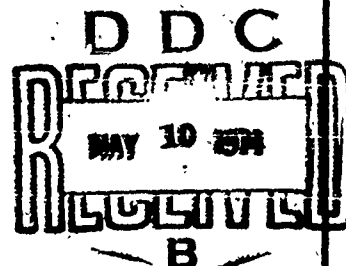
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AFATL-TR-74-30

NEW PYROTECHIC BINDERS-PHASE II

ROCKETDYNE DIVISION
ROCKWELL INTERNATIONAL

TECHNICAL REPORT AFATL-TR-74-30

JANUARY 1974



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AIR FORCE ARMAMENT LABORATORY

AIR FORCE SYSTEMS COMMAND • UNITED STATES AIR FORCE

EGLIN AIR FORCE BASE, FLORIDA

AD918935

New Pyrotechnic Binders-Phase II

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FOREWORD

This study was conducted by Rocketdyne Division, Rockwell International, 6633 Canoga Avenue, Canoga Park, California 91304, under Contract F08635-72-C-0143 with the Air Force Armament Laboratory, Eglin Air Force Base, Florida 32542. Mrs. Sandra M. Lefstad (DLIP) was Program Manager for the Armament Laboratory. This report covers work performed during the period from March 1973 to December 1973.

Principal investigator for Rocketdyne was Dr. C. L. Hamermesh with support from Mr. E. F. Witucki. Program Manager was Dr. B. L. Tuffly. The contractor report number assigned to this report is R-9419.

This technical report has been reviewed and is approved.



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ABSTRACT

Larger than laboratory-size batches of liquid high-oxygen-content polycarbonates and polyesters were prepared. Four different flare formulations were prepared from each of the polymers. Curing behavior, as well as the mechanical and burning behavior of the pyrotechnics after exposure to different environments, was evaluated. All four of the pyrotechnics containing polycarbonate performed in an outstanding manner, while only one of four formulations containing polyester performed satisfactorily.

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SECTION I

INTRODUCTION

Pyrotechnic compositions contain a very high proportion of solid ingredients. Small quantities of a liquid matrix material (binder) are included to: (1) provide fluidity for processing and (2) subsequent to processing, undergo crosslinking reactions to produce structures that will give the pyrotechnic structural integrity. At low binder levels, however, the pyrotechnic is still quite dry. Therefore, to obtain a coherent product, processing must consist of a series of pressings to produce the end item. This kind of manufacturing technique presents problems in sensitivity hazards during pressing as well as from the dusting that can occur when dry materials are processed.

Increasing the liquid binder content reduces both difficulties and improves processability. Thus, for example, in the LUU-2 flare, a higher quantity of a liquid polymer provides sufficient fluidity so that a tamp-cast product is obtained. However, this binder system has several shortcomings that limit its use in attaining a castable pyrotechnic. These include the relatively low oxygen content of the polymer (circa 40 percent) and the presence of undesirable carboxyl groups on the polymer that react with magnesium.

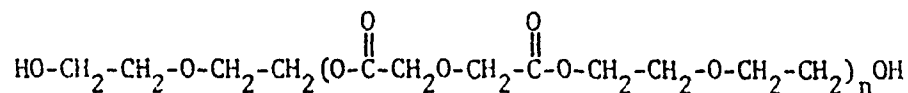
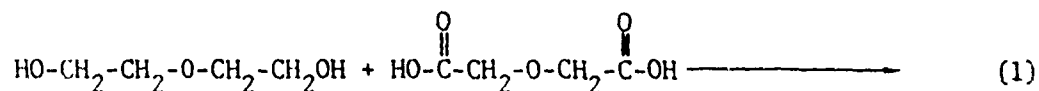
To obtain a castable system, larger quantities of a liquid binder must be employed. However, if the binder system is high in carbon and relatively low in oxygen content, upon combustion the carbon, which has not been oxidized, becomes incandescent and degrades both the color quality in a colored flare and the light output from an illuminating flare. Therefore, it is imperative that the polymer have an oxygen content high enough to combust all the carbon. In addition, the polymer must be compatible with considerations of cost and mechanical properties. This rules out the use of high-oxygen-content plasticizers that are costly and may also exude from the pyrotechnic and change the mechanical properties.

In the first phase of this program (Reference 1), polymer systems were selected on the basis of the following criteria:

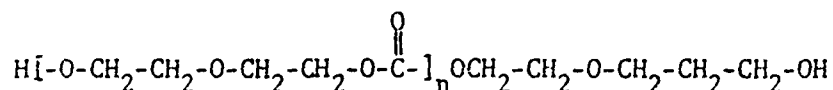
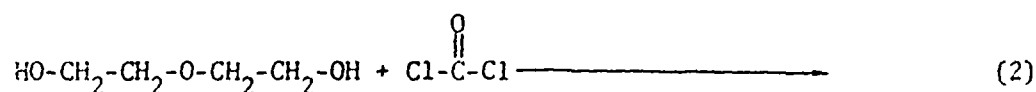
1. The polymers should have an oxygen content in excess of 40 percent and be of low viscosity and curable.
2. The curing of the polymer-curative combination should be compatible with conventional pyrotechnic manufacturing procedures.
3. The binder should be compatible with pyrotechnic ingredients.

Two low-cost, liquid-polymer systems were examined. They were:

1. The polyester (48-percent oxygen) formed from the reaction of diethylene glycol with diglycolic acid (Equation 1)



2. A poly (alkylene carbonate) (48-percent oxygen) prepared by the reaction of diethylene glycol with phosgene (Equation 2)



The bulk of the effort involved polymers of both types in which $n=5$ in Equations 1 and 2, respectively.

Curing behavior of these hydroxyl-terminated polymers was evaluated using a polyisocyanate, PAPI, as the cross-linking agent. Satisfactory cures were obtained even at ambient temperatures after 72 hours. The exotherm, observed under ambient temperature curing, was 1°F . These results, as well as the adequate pot life exhibited, indicated that the binders would be compatible with conventional pyrotechnic manufacturing procedures.

Mechanical properties of the cured binders were excellent with elongations of more than 500 percent and compression strengths in excess of 7500 psi. Shrinkage was less than 1 percent. The compatibility of these polymers with various pyrotechnic ingredients, as well as in pyrotechnic formulations, was evaluated. In vacuum stability tests at 70°C , less than 1.1 cc of gas was generated per gram of composition in 48 hours. This represented a high level of compatibility.

The results obtained in the first phase were a significant first step toward the development of practical, low-cost, castable pyrotechnic compositions. In this report, the contractor reports on the second phase, which involved evaluation of pyrotechnic compositions containing these polymers as part of the binder system.

SECTION II

SUMMARY

Thirty to forty pounds were prepared of each of two high-oxygen-content (48-percent) liquid polymers: (1) a polyester from diglycolic acid and diethylene glycol and (2) a polycarbonate from diethylene glycol and phosgene. The first compound was produced by a reaction performed in bulk, while the second was prepared in a solution of pyridine and benzene.

No difficulties were encountered in the scale-up preparations of the polyester. However, the first three large runs in the polycarbonate preparation gave low yields of product. This resulted from the failure to remove absorbed polymer from the pyridinium hydrochloride precipitate. This salt was formed by the reaction of pyridine with the HCl generated in the preparation of the polymer. In subsequent preparations, the work-up procedure was changed and 70-percent yields of polymer were obtained. Based on this new procedure, which involved a larger number of washes of the pyridinium hydrochloride with larger quantities of methylene chloride, it is estimated that with the proper equipment polycarbonate yields of 90 percent can be anticipated.

Pyrotechnic compositions analogous to the LUU-2 illuminating flare as well as the standard red, yellow, and green flares were prepared with each polymer. The polyisocyanate PAPI was used as a curative for both systems.

With the polycarbonate binder, formulations were obtained that would be castable with a minimal amount of pressure (<40 psi) at 160°F. The formulations were cured without gassing to give candles with good mechanical properties. When such candles were exposed to standard vibration or temperature shock tests, no evidence of grain growth or deterioration of mechanical properties was observed. Burning times for such candles after these exposures were essentially the same as for candles that had not been exposed. The only problem encountered with pyrotechnics containing the polycarbonate binder was the rapid viscosity build-up that hampered the processing of such compositions. This viscosity increase was probably due to the rapid reaction between the hydroxyl groups of the polymer and the aromatic isocyanate groups present in the PAPI curative.

By contrast, only the LUU-2 analog and the yellow flare composition could be prepared with the polyester binder and cured without gassing. Gassing occurred in the red and green flares composition despite all efforts to overcome this by changing the polymer-curative ratio, curing schedule, and/or catalyst content. On exposure to temperature shock, the yellow flare candles exhibited grain growth. Only the LUU-2 candles made with the polyester survived both the vibration and temperature shock tests without deterioration of mechanical properties. These candles exhibited no change in burning times as a result of these exposures.

Ninety-six candles (3 inches in height and 2-1/2 inches in diameter) containing the polycarbonate binder were prepared and submitted to the Air Force for evaluation. They included:

- a. 12 each of the red, yellow, and green formulations
- b. 12 each of five modifications of the LUU-2 formulation with binder levels of 8, 9, 10, 11, and 20 percent.

In a small mix, a castable LUU-2 composition was obtained at a binder level of 20 percent (polycarbonate 18 percent, PAPI 2 percent) when this formulation was processed at 160°F.

This program has demonstrated the potential of the liquid high-oxygen-content polycarbonate for use as a part of the binder system for pyrotechnic compositions. Additional work is needed for improving the pot life of such formulations, developing pyrotechnic compositions tailored for the high-oxygen content of the polymer, and increasing the information base in regard to polymer synthesis and scale-up.

SECTION III

DISCUSSION

This program was directed to develop and test preproduction quantities of new flares involving unique pyrotechnic binders. The work included:

1. Production of 30 to 40 pounds of polycarbonate and polyester derived from phosgene/diethylene glycol and diglycolic acid and diethylene-glycol, respectively.
2. Manufacture of four different pyrotechnic formulations containing these polymers.
3. Production of candles (3 inches in height and 2-1/2 inches in diameter) from such formulations.
4. Evaluation of the mechanical and burning behavior of such candles after exposure to different environmental conditions.
5. Manufacture of candles for submittal to the Air Force for evaluation.

POLYMER SCALE-UP

In the earlier effort (Reference 1), no more than 5 pounds of polyester or 2 pounds of polycarbonate were prepared in any one experiment. Therefore, to obtain the large quantities of polymer required for the current effort, it was necessary to scale-up these runs. A 50-liter resin reaction apparatus (kettle, Scientific Glass Catalog No. JR4110) was employed. This apparatus is long and cigar-shaped with a considerably smaller diameter-to-length ratio than the typical multi-necked resin flask used in the laboratory. Additionally, the stirrer shaft for the large reactor has two sets of four glass blades attached at right angles to the shaft. One set of blades is located at the bottom of the shaft, and the other is approximately two feet above the lower set. The effect of the change in apparatus employed on the product yield will be discussed below.

In the final phase of the earlier effort (Reference 1), attempts were made to reduce the viscosity of both the polyester and polycarbonate by changing the reaction stoichiometry as well as by replacement of diethylene glycol with triethylene glycol. Lower viscosity products were obtained, which gave lower viscosity mixes of the pyrotechnic formulation studied. However, there was evidence of solids separation in these mixes. In addition, it has been the contractor's experience that mixes of solid propellants having viscosities of several million centipoises can be cast. Since pyrotechnics are quite similar to solid propellants, it was the contractor's opinion that the higher viscosity formulations could be handled. Coupled with this conclusion was the fact that a larger amount of information was available in regards to these

polymers (Equations 1 and 2 where $n=5$, also see Characterization Report in Reference 1), as compared to the very limited amount available for the triethylene glycol polymers. This led to the decision that the higher viscosity polymers would be employed in the program described below.

Polyester

Thirty-eight pounds of this polymer were prepared in two runs. The procedure employed was analogous to that described in Reference 1 for the laboratory size batches. No difficulties were encountered in the scaled-up runs. Yields of polymer from the two large runs were 19 pounds per run or 97.5 percent of theoretical. The polymer viscosity of the blended batches was 33,100 cps (Brookfield Model LVT, Spindle No. 2, 23°C). When mixed with the PAPI curative at an isocyanate-to-hydroxyl ratio of 1, no gassing occurred and a cured product was obtained.

Polycarbonate

Unlike the polyester preparation, which is a reaction run in bulk, the polycarbonate is prepared in solution. Thus, a typical batch designed to yield 8 to 10 pounds of polymer contains 20 liters of a solution of benzene and pyridine. Therefore, a larger number of batches was required to produce the requisite amount of this polymer for subsequent studies than for the polyester system.

The first two scaled-up preparations were performed in a manner similar to that described for the smaller laboratory experiments (Reference 1) using a scale factor of 6. This method had resulted in 70 to 75 percent yields of polymer. However, in the larger runs only 5 and 4.25 pounds of polymer, corresponding to yields of 37 to 43 percent, were obtained.

Some differences were observed between the large runs and the laboratory preparations. The small runs were made in multi-necked, round-bottom flasks. In these cases, the experimental procedure was as follows: phosgene was flowed into the flask above the surface of the liquid and reaction of the glycol and the gas occurred at the interface. Hydrogen chloride, which is a by-product of this reaction, was removed by reaction with the pyridine. Visually, the solution first became opalescent (probably as the result of the formation of very fine particle size pyridinium hydrochloride). As the reaction progressed and more salt formed, the solution became cloudy and ultimately the hydrochloride precipitated from the reaction medium.

In the two larger scale runs, the series of events was accompanied by the formation of a very large quantity of solid at the surface of the liquid--so much, in fact, that the surface area where only liquid was present was markedly reduced. This difference was probably the result of the equipment used in the scaled-up runs. The stirring action in the 50-liter cylindrical kettle was much less efficient than in the round-bottom flask. The stirrer blades in

these larger runs were placed well below the surface so that agitation at the interface was minimal, and perhaps of greatest importance, the surface area-to-volume of the resin kettle was much lower than in the small, round-bottom flask.

To correct this situation, in the third run the stirrer shaft was moved so that the upper set of blades was located at the liquid interface. While this change did result in less accumulation of solid at the interface, only 5 pounds of polymer were obtained from the run. However, further insight into the cause of the low yield was obtained as a result of a change in work-up procedure that was made in this run.

In a typical polycarbonate preparation, after stirring had been stopped, the pyridinium hydrochloride settled to the bottom of the flask and a clear solution was present above the salt. In the laboratory runs and the first two large preparations, the following procedure was employed:

1. Filter the solution.
2. Wash the filter cake twice with methylene chloride.
3. Combine the filtrate with the washings and continue the work-up.

In the third large run, the methylene chloride washings were worked up separately from the filtrate. Four pounds of polymer (80 percent of the total yield) were obtained from the washings and only one pound from the filtrate. It therefore appeared that the low yield of polymer in the first two large runs was not due solely to failure of the phosgene to react quantitatively with the glycol, but also to the inadequacy of the work-up procedure in removing absorbed polymer from the pyridinium hydrochloride.

To check out this hypothesis, a fourth large run was made in which (1) the stirrer blades were kept at the interface (as in run No. 3) and (2) the work-up procedure was modified in that additional washings of the filter cake with large quantities of methylene chloride (circa 0.5 gallon per wash) were performed. This procedure added some minor difficulties in that the pyridinium salt is solubilized by the mixture of solvents, and on stripping the washings, solid precipitated out of the solution. This was corrected by filtering off the solid before final concentration. Despite this added operation, a total of 8 pounds (69 percent yield) of polymer was obtained from run No. 4; seven pounds were derived from the methylene chloride washings. A fifth run confirmed these results in that approximately 9 pounds (78 percent yield) of polymer were obtained; the vast bulk came from the washings. (The results of all scale-up preparations are summarized in Table I.)

From the results of runs No. 3, 4 and 5, it is the contractor's opinion that the reaction of phosgene and glycol is probably highly efficient and, with the proper equipment and work-up procedure, polymer yields of 90 percent of theoretical are possible. In the Experimental Section of this report, the recommended preparative and work-up procedures are described.

TABLE I. SCALE-UP PREPARATION OF POLYCARBONATE

Run number	Polymer, pounds	Yield, percent	Remarks
1 ^a	5.0	43	Standard procedure (Reference 1) was used. Stirrer blades were below surface of liquid. The filtrate and methylene chloride washings (2 times) of the pyridinium hydrochloride were combined, and the polymer was isolated by concentration.
2 ^a	4.25	37	Standard procedure (Reference 1) was used. Stirrer blades were below surface of liquid. The filtrate and methylene chloride washings (2 times) of the pyridinium hydrochloride were combined, and the polymer was isolated by concentration.
3 ^a	5.0	43	Stirrer blades were at the interface. The methylene chloride washings were worked up separately. Four pounds of polymer were recovered from the washings.
4 ^a	8.0	69	Stirrer blades were at the interface. Filter cake was washed more extensively. Methylene chloride washings were worked up separately, and 7 pounds of polymer were isolated from the washings.
5 ^a	9.0	78	Stirrer blades were at the interface. Filter cake was washed more extensively. Methylene chloride washings were worked up separately, and 7 pounds of polymer were isolated from the washings.
^a 4584g Diethylene glycol, 7200 ml pyridine, 12,240 ml benzene, and 3564g phosgene.			

As a final check on the suitability of the polymers for use in pyrotechnic formulations, samples of polymer from each of the five large runs were mixed with the requisite quantity of PAPI (NCO/OH=1) and the curing behavior of the mixture was evaluated. In some cases, gassing was observed. Since this is indicative of the presence of moisture, all polymer batches were stripped at full vacuum at 90° to 100°C for 2 to 3 hours before use. After this procedure, curing with PAPI occurred without any gassing.

PYROTECHNIC PREPARATION AND EVALUATION

The second task in this effort involved:

1. Preparation of 12 candles (3 inches in height and 2-1/2 inches in diameter) of each of four pyrotechnic formulations containing each of the polymers.
2. Evaluation of the mechanical and burning behavior of these candles after manufacture as well as after exposure to vibration or temperature shock.

The four pyrotechnic compositions selected for study were the LUU-2 illuminating flare and the standard red, yellow, and green flares. The specifications for the solid ingredients were provided by the Air Force Program Monitor and are included in Table II.

Polycarbonate Containing Formulations - Preparation

For all compositons shown in Table II, small hand mixes were made and their curing behavior was evaluated. If this was satisfactory, a larger batch was prepared from which the test candles were produced.

TABLE II. PYROTECHNIC FORMULATIONS

<u>LUU-2 Illuminating Flare</u>	<u>Percent</u>	<u>Yellow Flare</u>	<u>Percent</u>
Magnesium ^a	61	Magnesium ^a	15
Sodium Nitrate ^b	30	Sodium Nitrate ^b	65
Binder	9	Binder	20
<u>Green Flare</u>	<u>Percent</u>	<u>Red Flare</u>	<u>Percent</u>
Barium Chlorate ^c	12	Strontium Nitrate ^c	46
Barium Carbonate ^c	60	Strontium Chloride ^c	12
Binder	28	Ammonium Perchlorate ^d	18
		Magnesium ^a	4
		Binder	20
^a 50-200 mesh ^b 1:1:1 weight ratio of 50, 150, 250 μ sizes ^c Used as received ^d 200 μ			

1. LUU-2 Illuminating Flare

As expected, with only 9-percent binder (6.75 percent polymer, 2.25 percent PAPI), a noncastable but pressable composition was obtained. After 16 hours at ambient temperature and 8 hours at 160°F, a coherent non-gassing product was obtained. This binder combination was used in preparing the candles.

2. Yellow Flare

At ambient temperature, the yellow flare formulation (16 percent polymer, 4 percent PAPI) was not sufficiently fluid to be castable. However, it was concluded that such a mix would with mild pressure (<40 psi) be castable if processed at 140° to 160°F. Using the same cure schedule as with the illuminating flare, a well-cured non-gassing product resulted. This formulation was employed in preparing the 12 candles for evaluation.

3. Green Flare

Because the binder level for the green flare is so high (28 percent), it was not surprising that an extremely fluid castable composition was obtained at that level (22.5 percent polymer, 5.5 percent PAPI). Curing was excellent (same cure schedule as above), and no gassing occurred. The candles were made using this recipe.

4. Red Flare

In small mixes of the red flare composition, two levels of the polymer-curative combination, as well as another curative, were examined. The binder combinations studied were:

- a. Polymer 18 percent, PAPI 2 percent
- b. Polymer 16 percent, PAPI 4 percent

Neither mix gave a castable system at ambient temperature. However, at 160°F, a pressure castable system should be obtained.

In another experiment, part of the polyisocyanate PAPI was replaced with a diisocyanate, isophorone diisocyanate (IPDI, H. Stinnes, Germany). The objective here was to reduce the mix viscosity and improve castability. For this formulation (17 percent polymer, 2 percent IPDI, and 1 percent PAPI), a more fluid but non-castable system was obtained at ambient temperature.

After 72 hours in a 160°F oven, all three red flare formulations had cured without gassing. However, the formulations with the 2 percent PAPI level and the mixed isocyanates were somewhat soft. Therefore, the formulation with 16 percent polymer and 4 percent PAPI was used in preparing the 12 candles. A well-cured, non-gassing product was obtained.

The pot life was marginal for all of the formulations used in preparing the candles (Table III). That is, a rapid build-up of viscosity was observed that undoubtedly would hamper large scale production. Part of this difficulty is due to the rapid reaction between the hydroxyl groups at the ends of the polymer and the aromatic isocyanate groups in the PAPI. The rest of the problem may be due to the processing being carried out at ambient temperature. In the Recommendations Section of this report, several approaches are discussed for improving the pot life and castability of these systems.

TABLE III. POLYCARBONATE CONTAINING FORMULATION
USED IN CANDLE PREPARATION

<u>LUU-2 Illuminating Flare</u>	<u>Percent</u>	<u>Yellow Flare</u>	<u>Percent</u>
Magnesium ^a	61	Magnesium ^a	15
Sodium Nitrate ^b	30	Sodium Nitrate ^b	65
Polycarbonate	6.75	Polycarbonate	16
PAPI	2.25	PAPI	4
<u>Green Flare</u>	<u>Percent</u>	<u>Red Flare</u>	<u>Percent</u>
Barium Chlorate ^c	12	Strontium Nitrate ^c	46
Barium Carbonate ^c	60	Strontium Chloride ^c	12
Polycarbonate	22.5	Ammonium Perchlorate ^d	18
PAPI	5.5	Magnesium ^a	4
		Polycarbonate	16
		PAPI	4
^a 50-200 mesh ^b 1:1:1 weight ratio of 50, 150, 250 μ sizes ^c Used as received ^d 200 μ			

Polycarbonate Containing Formulations - Evaluation

Evaluation of the candles involved the following:

4 were exposed to the temperature shock test

4 were exposed to the vibration test

4 were kept as controls.

The temperature shock test employed was Method 503 of Military Standard 810B and consisted of the following exposure for the candles:

1. Day 1 and 2: 4-hour exposure at 160°F, 4 hours at -65°F, and 1 hour at 160°F.
2. Day 3: 4 hours at 160°F and 4 hours at -65°F. After this exposure, the candles were examined visually for evidence of grain growth as well as any deterioration of mechanical properties.

The vibration test specified in the contract was to be in accordance with Method 514.1 of Military Standard 810B. Although the contractor's vibration test equipment (a Syntron shaker) does not meet this standard in that the frequency of the vibration is somewhat lower, the Air Force Program Manager agreed to accept the contractor's vibration test. The candles were placed on the Syntron shaker and vibrated for one hour under full load at 90 amperes (standard test requires 105 amperes). The criteria for successful resistance of the candles to vibration were no grain growth or deterioration of mechanical properties.

Those candles that successfully survived the vibration and temperature shock tests, as well as the 4 control candles, were then burned. The ignition device employed nichrome wires that were laid across the top of the candle. Thin slabs of solid propellant were placed between the wires and the candle. When current was passed through the wires the propellant ignited, which ignited the candle in turn. Burn times were measured as the time elapsed from the first observation of intense flame to the point of extinguishment of this flame.

All pyrotechnic candles containing the polycarbonate binder exhibited an excellent level of resistance to both temperature shock and vibration. No gassing was observed, nor was there any visual evidence of mechanical deterioration of these candles. The burning behavior of these candles, as well as those used as controls, are shown in Table IV. From this data, it is evident that neither vibration nor temperature cycling significantly affected the burning behavior of the pyrotechnics containing the polycarbonate binder.

Polyester Containing Pyrotechnics - Preparation

1. LUU-2 Illuminating Flare

A non-castable system that cured without gassing was obtained when the binder consisted of 7.2 percent polymer and 1.8 percent PAPI. This formulation was used for preparation of the test candles.

TABLE IV. BURNING BEHAVIOR OF PYROTECHNIC
CANDLES CONTAINING POLYCARBONATE

Composition	Exposure	Burning time, seconds ^a
LUU-2	None	19.0
	Vibration	17.4
	Temperature Shock	18.0
Yellow Flare	None	149.4
	Vibration	144.8
	Temperature Shock	153.6
Green Flare	None	245.2
	Vibration	171.0
	Temperature Shock	262.2
Red Flare	None	169.2
	Vibration	171.0
	Temperature Shock	160.9
^a Average of four tests		

2. Yellow Flare

A non-castable yellow flare formulation that cured without gassing was obtained when the binder consisted of 18 percent polymer and 2 percent curative. At 16 percent polymer and 4 percent PAPI, gassing occurred during the curing cycle. The former binder composition was used for candle preparation.

3. Red and Green Flare

Difficulties were encountered in obtaining suitable candles for the red and green compositions. Regardless of the binder level, curative content, presence or absence of a cure catalyst (i.e., ferric acetylacetonate, FeAA), both the red and green formulations containing the polyester binder gassed on curing. Changes in curing schedule, such as maintaining the formulations at ambient temperature for periods up to 72 hours, did not correct this situation. Because this problem could be related to moisture present in the solid ingredients, these materials were dried under full vacuum at temperatures up to 150°C. Despite these treatments, gassing still occurred. Therefore, no candles of either the red or green composition were prepared.

The source of the difficulties encountered was not conclusively established. However, the polyester does have a very small number of free carboxyl groups (acid number = 20). If moisture is present in the mix, mineral acid may be generated by reaction with the strontium or barium salts. This acid may, in turn, degrade the polyester, particularly at elevated temperatures, causing gas to evolve. This hypothesis has been confirmed to some extent by laboratory experiments in which the cured polyester has been degraded under relatively mild conditions (up to 60°C) in the presence of mineral acids.

Polyester Containing Pyrotechnics - Evaluation

1. LUU-2 Illuminating Flare

The LUU-2 flare composition containing the polyester survived both the vibration and temperature shock tests described above with no evidence of mechanical deterioration or grain growth. Burning behavior of these candles, as well as the control candles, are shown in Table V. It is apparent that the exposure had little effect on burning behavior.

TABLE V. BURNING BEHAVIOR OF LUU-2
FLARE CONTAINING POLYESTER

Treatment	Burning time, seconds ^a
None	19.3
Vibration	19.2
Temperature Shock	18.0
^a Average of 4 tests	

2. Yellow Flare

When the yellow flare compositions were exposed to temperature shock, grain growth was observed. Therefore, further testing of this system was abandoned.

PREPARATION OF CANDLES FOR SUBMITTAL TO THE AIR FORCE

The final task in this program was the preparation for submittal of 96 candles to the Air Force for evaluation. Before doing this, a meeting was held with personnel of the Pyrotechnics Branch of the Air Force Armament Laboratory to review the results discussed above. It was agreed that no further work should be done during this program on formulations containing polyester and that candles be made only with the polycarbonate binder. The 96 candles to be submitted would consist of:

12 each of the red, yellow, and green flares

12 each of five modifications of the LUU-2 compositions in which the binder levels would be 8, 9, 10, 11, and 12 percent.

The objective of the latter effort was to measure the effect of the high-oxygen-content binder on burning behavior, as well as to determine if a castable composition could be obtained at the higher binder levels.

Preparation of the red, yellow, and green flares, as well as the lower binder level variations of the LUU-2 flare, proceeded with no difficulties. However, hand mixes of the 12 percent binder system composition were not castable. Therefore, formulations with 15 , 17 , and 20 percent binder were examined. Only at 20-percent binder (18 percent polymer, 2 percent PAPI) was a castable system obtained, and this required processing at 160°F and the use of pressure (<40 psi) in casting. Based on these results, discussions were held with the Air Force Program Monitor, and it was agreed that the 20 percent binder system would be substituted for the 12 percent system. When the large batch of the former was prepared, failure of a hot water boiler precluded processing at 160°F. To avoid loss of the candles, they were press cast at ambient. A coherent non-gassing product was obtained.

The 96 candles have been submitted to the Air Force for evaluation.

SECTION IV

CONCLUSIONS

Additional evidence of the potential of the polycarbonate binder in pyrotechnic applications has been generated in that formulations can be made with this binder that are castable with minimal pressure and at reasonable temperatures. These formulations cure without gassing to give products with good mechanical properties. Such pyrotechnics are unaffected by exposure to either vibration or temperature shock in regard to retention of structural integrity or burning behavior.

However, several problem areas still exist in regard to the use of the polycarbonate binder in pyrotechnics. They are:

1. The rapid viscosity build-up that limits the pot life of such compositions.
2. The failure to formulate pyrotechnic compositions that are designed to make optimum use of the high-oxygen content of the polymer.
3. The minimal information base presently available in regard to both the polymer synthesis and scale-up.

The polyester binder will require additional effort before it can be employed successfully in pyrotechnics composition.

SECTION V

RECOMMENDATIONS

It is recommended that additional efforts be made in the area of the polycarbonate binder with the objective of:

1. Developing castable formulations with long pot lives.
2. Developing formulations tailored for high-oxygen-content binders.
3. Synthesizing binders of even higher oxygen content.
4. Obtaining better control of the polymer synthesis and scale-up procedure.

IMPROVED CASTABILITY AND POT LIFE

For improved castability and pot life, a study should be made of the effect of partial or total replacement of the PAPI curative with a diisocyanate, preferably one of higher oxygen content than in PAPI (12 percent) and also of the aliphatic isocyanate type. The latter would be preferred in that such species are reported to be less reactive with hydroxyl groups than the aromatic isocyanate groups present in PAPI. (Some work on this subject has been done at the contractor's facility.) Polycarbonates of lower viscosity than the polymers studied in this effort should be prepared and formulated into pyrotechnics to evaluate the effect of the lower viscosity on castability. Finally, a study should be made of means of curing hydroxyl-terminated polymers by means of reactions that do not involve isocyanates. For example, curing with low molecular weight diepoxides is a distinct possibility.

TAILORING OF PYROTECHNIC FORMULATION

Development of formulations tailored for the high-oxygen content of the binders should be directed toward (1) a castable LUU-2 flare and (2) a red flare for air-sea rescue operations. Parameters to be studied would include compositional changes, the effect of the type and amount of solid ingredients in the formulations on the curing of the binder, and the effect of sources of halogen other than strontium chloride on the color quality for the red flare.

NEW HIGH-OXYGEN-CONTAINING BINDERS

Process improvements in regard to the polymer synthesis should involve a study of the effect on yield of polymer and polymer viscosity of the stirring device employed, the solvent, and the work-up procedure. In addition, other stoichiometric ratios of diethylene glycol and phosgene should be evaluated, since little is known concerning the utility of such polymers for pyrotechnic applications. Finally, an effort should be made to prepare polycarbonates of even higher-oxygen content (up to 54.5 percent) by reacting ethylene glycol with phosgene.

SECTION VI

EXPERIMENTAL

MATERIALS

1. Diglycolic acid - Practical grade, Columbia Chemical
2. Diethylene glycol - Chemical grade, Eastman
3. Phosgene - Chemical grade, Matheson
4. Benzene - Chemical grade, Eastman
5. Pyridine - Chemical grade, Eastman

All chemicals were used as received.

PREPARATION OF POLYESTERS

In preparation of the polyesters, 5252.5g (49.5 moles) of diethylene glycol and 5500g (41.3 moles) of diglycolic acid were placed in the 50-liter flask previously described, which was equipped with a stirrer and thermometer. The mixture was heated to 180°C and maintained at this temperature. Samples were removed hourly until the acid number of the product reached 20. The acid number was determined by dissolving a weighed sample of the polymer in equal volumes of benzene and methanol. A titration indicator (10 drops of bromothymol blue) was added. The solution was titrated with standard 0.5 N potassium hydroxide. To calculate the acid number, the following equation was used:

$$\text{Acid Number} = \frac{(\text{ml of KOH}) (\text{mg of KOH per ml}^*)}{\text{Wt of sample}}$$

When the acid number had reached the desired value, the reaction was terminated. To ensure that no water remained in the polymer, the product (a light-yellow-to-brown-colored liquid) was placed on a Rinco evaporator and stripped at full vacuum at 90°C for 3 hours.

PREPARATION OF POLYCARBONATES

In preparation of the polycarbonates 4584g (49.5 moles) of diethylene glycol, 7200 ml pyridine, and 12,240 benzene were placed in the 50-liter reaction apparatus previously described, which was equipped with a stirrer, thermometer, gas inlet, and outlet attachments. A gas-metering apparatus was connected upstream from the gas inlet. A bubble device was located downstream of the gas outlet. The apparatus was swept with nitrogen for approximately 10 minutes to

*For 0.5 N KOH, this equals 28.

remove any moisture. The reaction mixture was cooled to 10°C, and 3564g (41.3 moles) of phosgene was bubbled into the flask (above the liquid) at such a rate that the reaction temperature remained below 15°C. The reaction became cloudy as the pyridinium hydrochloride was formed and ultimately precipitated from the solution. After the addition of phosgene was complete, the reaction mixture was allowed to warm to ambient temperature and was then heated at 80°C for 1 hour. Finally, the reaction was stirred overnight at ambient temperature under a slow nitrogen purge.

The reaction mixture was filtered under a blanket of nitrogen to remove pyridinium hydrochloride. The filter cake was washed at least 3 times with 0.5 gallon of methylene chloride per wash. If the washings were cloudy, they were filtered.

Although the filtrate and washings were worked up separately, the procedure employed was identical. The liquid was stripped first with a nitrogen sweep and finally in the Rinco evaporator at full vacuum at 55°C for 3 hours. The resulting liquid was dissolved in methylene chloride and washed several times with equal volumes of a 1-percent sodium hydroxide solution until the pH of the bottom layer containing the polymer was 8. This layer was then washed with water to remove traces of the base. The resulting liquid was then reduced in volume under a nitrogen sweep and finally stripped at 90° to 100°C under full vacuum on a Rinco evaporator for 3 hours to yield liquids with a yellow cast.

PREPARATION OF CANDLES

A typical candle preparation was that of the LUU-2 analog. Polycarbonate (202.5g) and 67.5g of PAPI were placed in a 5-gallon Baker Perkin vertical blade mixer and stirred for five minutes. The mixing action was stopped, the mixer lowered, and 915g of magnesium and 450g of sodium nitrate added. The batch was mixed for 5 minutes after which an additional 9.5g of magnesium and 450g of sodium nitrate were added and mixed for 10 minutes. The relatively dry mixture was press cast into metal tubes (3 inches high and 2-1/2 inches in diameter), allowed to remain at ambient temperature overnight, and then placed in a 160°F oven for 16 hours.

REFERENCES

1. Hamermesh, C. L. and E. F. Witucki, "New Pyrotechnics Binders," AFATL-TR-73-13, January 1973.

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Security Classification

DOCUMENT CONTROL DATA - R & D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY (Corporate author) ROCKETDYNE DIVISION ROCKWELL INTERNATIONAL CORPORATION 6633 Canoga Avenue, Canoga Park, California 91304		2a. REPORT SECURITY CLASSIFICATION Unclassified
		2b. GROUP
3. REPORT TITLE NEW PYROTECHNIC BINDERS - PHASE II		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report - March 1973 to December 1973		
5. AUTHOR(S) (First name, middle initial, last name) C. L. Hamermesh E. F. Witucki		
6. REPORT DATE January 1974	7a. TOTAL NO. OF PAGES 28	7b. NO. OF REFS 1
8a. CONTRACT OR GRANT NO. F08635-72-C-0143	9a. ORIGINATOR'S REPORT NUMBER(S) R-9419	
b. PROJECT NO. 2563		
c. Task No. 06		
d. Work Unit No. 08	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) AFATL-TR-74-30	
10. DISTRIBUTION STATEMENT Distribution limited to U. S. Government agencies only; this report documents test and evaluation; distribution limitation applied January 1974. Other requests for this document must be referred to the Air Force Armament Laboratory (DLIP), Eglin Air Force Base, Florida 32542.		
11. SUPPLEMENTARY NOTES Available in DDC		12. SPONSORING MILITARY ACTIVITY Air Force Armament Laboratory Air Force Systems Command Eglin Air Force Base, Florida 32542
13. ABSTRACT Larger than laboratory-size batches of liquid high-oxygen-content polycarbonates and polyesters were prepared. Four different flare formulations were prepared from each of the polymers. Curing behavior, as well as the mechanical and burning behavior of the pyrotechnics after exposure to different environments, was evaluated. All four of the pyrotechnics containing polycarbonate performed in an outstanding manner, while only one of four formulations containing polyester performed satisfactorily.		

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